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BROAD FEATURES OF SURFACE OZONE VARIATIONS OVER INDIAN REGION

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ABSTRACT

Surface ozone concentration at three Indian stations - New Delhi (28.6°N), Pune (18.5°N) and Thiruvananthapuram (formerly Trivandrum) (8.3°N) - has been measured since 1973 with the help of an electrochemical continuous ozone recorder. These stations show diurnal, seasonal and annual cycles in surface ozone. Daily changes show that the minimum value occurs at sunrise and maximum in the afternoon. As regards seasonal variations, Thiruvananthapuram and Pune have a minimum value during monsoon season (June to August) while at New Delhi the minimum value occurs in January. However, New Delhi also records low ozone amount during monsoon season identical to the amounts shown at Thiruvananthapuram and Pune. The annual cycles at these stations have been compared with similar measurements in the northern and southern hemispheres. The Indian measurements agree well with the annual cycles at these stations. Further, the analysis of the Indian data indicates that the major contribution in surface ozone comes from the natural sources like stratospheric-tropospheric exchange, turbulence and mixing in the boundary layer; however, a small contribution from anthropogenic sources cannot be ruled out at Pune and probably at New Delhi, especially in winter and summer seasons.

1. INTRODUCTION

The importance of ozone measurement near the ground and in the troposphere has been realised in last two decades. Ozone is one of the most important trace species in the troposphere, which can directly affect climate through the absorption of infra-red radiation (Fishman et al., 1979). Increasing concentration of tropospheric ozone has been reported, especially in the northern hemisphere, in recent times (Logan (1985), Angell et al. (1983), Oltmans and Komhyr (1986), Bojkov (1986), Penkett (1988)). Ozone as a greenhouse gas is influencing the outgoing radiation budget and as a consequence the climate. There is much discussion on the relative contributions to the surface ozone concentration, from the stratosphere due to natural processes and from the troposphere due to human activities (Levi et al., 1985).

Surface ozone measurements have been made and examined by various workers, Oltmans and Komhyr (1986) at four land-based stations of Barrow, Alaska (71°N); Mauna Loa, Hawaii (19.5°N); American Samoa (14°S) and the South Pole (90°S), Low P.S. (1990) at Hohenpeissenberg and Arkona in Germany and Galbally et al. (1980) in Australia. Measurements of surface ozone concentration over ocean have been reported by Routhier et al. (1980), Liu et al. (1983) and Piotrowicz (1986).

Surface ozone measurements using an electrochemical continuous ozone sensor (Sreedharan and Tiwari, 1971) were started at Pune (18.5°N, 73.8°E) in 1970 and the diurnal, seasonal and short-term variations have been described on the basis of records obtained during 1972-73 (Tiwari and Sreedharan, 1973). Since 1973, the measurements were extended to two more stations namely, New Delhi (28.6°N, 77.2°E) and Thiruvananthapuram (8.3°N, 76.6°E). Hourly data at these stations have been computed from the continuous records of 1973, 1974 and 1975 and again for 1983, 1984 and 1985. Broad features of the surface ozone concentration as related to seasonal (winter, summer, monsoon and post-monsoon), diurnal, latitudinal and time-scale changes over the Indian region are described and the possible causes of these variations discussed in the present paper. The contribution of tropospheric production, if any, has also been examined from the above data.

2. VARIATION IN SURFACE OZONE CONCENTRATION OVER INDIAN REGION

Tropospheric ozone absorbs the outgoing longwave radiation from the earth, thereby contributing to the greenhouse effect. Till sixties, the tropospheric concentration of ozone was very low and its contribution to greenhouse warming was thought to be insignificant. It was also generally accepted until sixties that the main source of tropospheric ozone is from the middle and the upper stratosphere where it is produced by the photochemical reaction of ultraviolet radiation with the oxygen molecules. From the stratosphere, this heavier gas trickles down through the tropopause by various mixing processes associated with cyclonic circulations, jet streams and through tropopause breaks. Junge

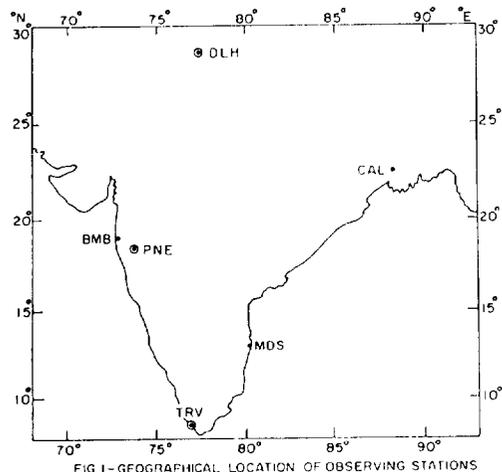
(1962) showed that the rate of production of ozone in the stratosphere and its rate of destruction near the ground are same, thereby supporting that the stratosphere is the main source of tropospheric (surface) ozone.

In recent years, increasing trends in surface ozone concentrations have been reported at Hohenpeissenberg (47.8°N) and Arkona (54.7°N) by Low P.S. (1990). Bojkov (1988) and Penkett (1988) have also reported that over most of the northern hemisphere surface ozone concentrations have increased. This increase in surface ozone is attributed to increasing anthropogenic sources. Over Indian subcontinent, the daily and seasonal variations in surface ozone indicate a good correlation with changes in wind speed, surface temperature and overall mixing conditions in the boundary layer. However, some contribution by man-made sources cannot be ruled out especially after 1980.

2.1 Seasonal changes at the Indian stations

Before describing the seasonal behaviour at Thiruvananthapuram, Pune and New Delhi, it would be appropriate to describe the topography and surroundings of these stations. New Delhi is a densely populated city in the plains of northern India and is affected by extreme summer and winter climates. Pune is situated on the Deccan Plateau on the eastern side of Western Ghats, at a height of about 600 m (asl) with moderate climate changes throughout the year. The city is relatively clean, but Bombay - a highly industrialised and populated city - is located about 200 km away in West-North-West direction. The industrial belt at Pune extends in N-NE sector about 5 km away from the observational site. Thiruvananthapuram is a tropical coastal station with natural green surroundings with less population and few industries. This can be treated as a background unpolluted station. Fig. 1 shows the geographical locations of the three stations in the Indian subcontinent.

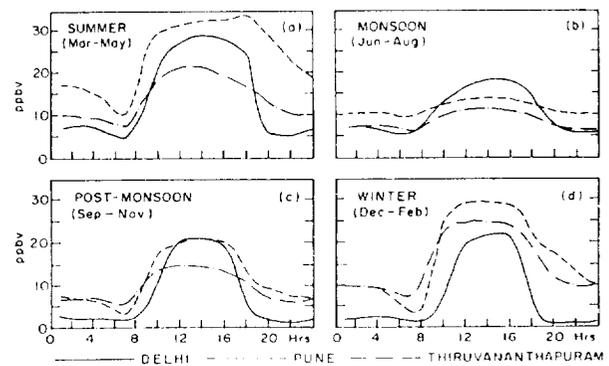
Fig. 2 shows the hourly variations of surface ozone at New Delhi, Pune and Thiruvananthapuram for the four seasons - summer



(March-May), monsoon (June-August), post-monsoon (September-November) and winter (December-February). The hourly values have been averaged for each month and the mean hourly values for the four seasons computed from three years' data (1983, 1984 and 1985) have been plotted. The graphs for all the three stations clearly bring out that a minimum concentration of surface ozone is attained in the morning around 0700 (LST) coinciding with sunrise and a maximum is attained in the afternoon between 1400 and 1600 (LST). The occurrence of daily minimum and maximum ozone amount coincides with the lowest and the highest convection and turbulent mixing in the boundary layer respectively. Lowest values at Pune and Thiruvananthapuram are of the order of 5 to 8 ppbv, while night time value at New Delhi is lower compared to Pune and Thiruvananthapuram with minimum value up to 5 ppbv.

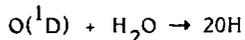
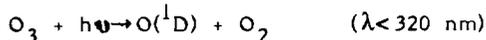
2.1.1 Hourly variation during summer season

Mean hourly changes in surface ozone during summer season are shown in Fig. 2a. Night time values are uniformly low at New Delhi and are varying between 5 and 7 ppbv. Thiruvananthapuram night time values are also low, about 10 ppbv, while Pune shows higher ozone concentration, of the order of 15 ppbv or more, during night hours. Day time values are the highest at Pune (30-34 ppbv) followed by New Delhi (25-29 ppbv) and the lowest value is observed at Thiruvananthapuram (20-22 ppbv). Further, the gradient of forenoon rise is the highest at Pune followed by New Delhi and is the lowest at Thiruvananthapuram. Pune and New Delhi forenoon records indicate that a cool and stable layer is formed near the ground preventing the free mixing across it. Pune record has one peculiarity that maximum value is observed around 1800 h. in the evening. The wind speed record also indicates an increase in the evening hours associated with ozone maxima. This maximum value around 1800 h. can be due to subsidence of tropospheric air on account of sudden cooling or due to air blowing from a highly polluted area and hence having high value of ozone concentration.



2.1.2 Hourly changes during monsoon season

Ozone concentration during monsoon season (June-August) depicts low ozone value with decreased diurnal changes (Fig. 2b). The lowest value in the morning at all the three stations is between 5 and 10 ppbv but the highest value in the afternoon shows higher value with increasing latitude. During monsoon season, the air circulation over the Indian subcontinent is prevailing south-westerly flow from Arabian Sea and is redirected from SE direction in the Bay of Bengal along monsoon trough. The tropospheric air mass over the entire country is the monsoonal flow from low latitudes and partly from the southern hemisphere. The low concentration of ozone may be due to destruction by H_2O molecules which are available in abundance during this season by following reactions (Fishman et al. (1977), Logan et al. (1981):



The low ozone concentration may also be due to the effect of air from the southern hemisphere tropics, which is poor in ozone (Winkler P., 1989).

2.1.3 Hourly changes during post-monsoon season

After the monsoon season, diurnal changes have started increasing (Fig. 2c). All the three stations show higher difference between night and day values; night time values have decreased and the day time values increased. Night value is the lowest at New Delhi followed by Thiruvananthapuram and is the highest at Pune. Day time values are the lowest at Thiruvananthapuram while the concentrations at New Delhi and Pune are almost equal (however, day mean value is higher at Pune).

2.1.4 Hourly changes during winter season

Hourly changes in surface ozone during winter season (December-February) are shown in Fig. 2d. New Delhi shows near zero value (about 2 ppbv) throughout the night; so also the day time value is low, about 22 ppbv, followed by Thiruvananthapuram, while both day and night ozone amounts are the highest at Pune.

Day and night low values at New Delhi can be expected from the fact that during winter season it experiences extreme cold climate and the maximum temperature during winter is nearly equal to the minimum temperature obtained at the other two stations, Pune and Thiruvananthapuram. The difference between day's maximum and minimum ozone amounts is the highest at Pune (about 25 ppbv). The trend of decreasing

ozone concentration in the evening hours at Pune is not as sharp as at Thiruvananthapuram and New Delhi, indicating thereby that the replenishment of ozone near the ground continues at a faster rate during evening and early part of the night at Pune compared to New Delhi and Thiruvananthapuram. This appears to be due to its location on a plateau 600 m high and its nearness to the top of the boundary layer. Only in early hours between 0600 and 0800 it shows that the supply from the free troposphere is cut off on account of formation of cool and stable layer and during that time ozone values at Pune, New Delhi and Thiruvananthapuram are identical. This behaviour in ozone changes at Pune is further confirmed from the record of summer season (Fig. 2a). The trend in ozone changes at Pune during winter and summer seasons, especially the slow fall in the evening and early part of night, calls for a subsidence motion or transport of ozone rich air from polluted atmosphere.

To summarise the seasonal changes, the three years' (1983-1985) mean data has been examined pertaining to seasonal mean value (Fig. 3a), day time value (0800 to 1900 h.) (Fig. 3b), night time value (2000 to 0700 h.) (Fig. 3c) and the difference between day and night values (diurnal change) (Fig. 3d). These values are plotted corresponding to the respective latitudes of the three stations.

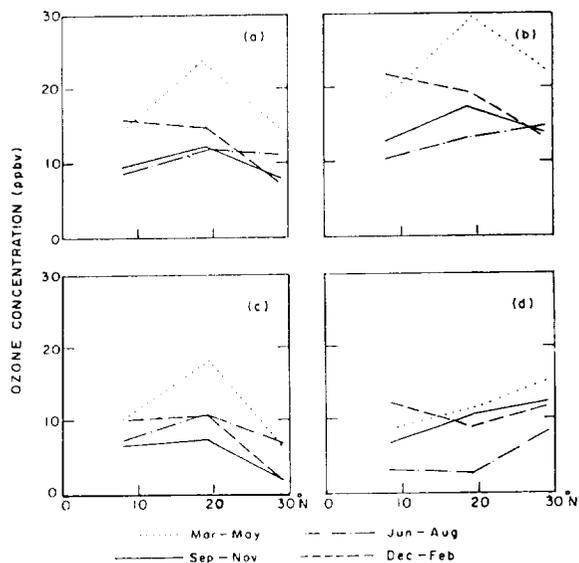


FIG. 3 - LATITUDINAL VARIATION OF SURFACE OZONE DURING FOUR SEASONS (1983 - 1985 Mean) (a) Seasonal mean, (b) Day time value, (c) Night time value, (d) Diurnal change

The seasonal mean (Fig. 3a) shows that during monsoon months there exists a latitudinal gradient between Thiruvananthapuram and Pune (from 8° to 18°N); thereafter the value is same up to 28°N (New Delhi). During winter, there appears to be a reversal of surface ozone

gradient from 30°N to 8°N, i.e. the daily mean surface ozone decreases as latitude increases. During post-monsoon and summer seasons, Thiruvananthapuram and New Delhi show identical trends but Pune shows a higher concentration, the mean value during post-monsoon being lower than summer at all the three stations. Further, the absolute value of surface ozone at Thiruvananthapuram and New Delhi varies between 8 and 15 ppbv while at Pune the variation is from 12 to 24 ppbv.

The average concentration during day (mean of hourly values between 0800 and 1900 h.) shows a linear latitudinal gradient during monsoon season and a reversed latitudinal gradient during winter, while during rest of the seasons Pune has the highest value, Thiruvananthapuram and New Delhi have nearly same value in post-monsoon, but a slight higher value is seen at New Delhi during summer. Day values at New Delhi range between 12 and 22 ppbv, at Thiruvananthapuram from 10 to 19 ppbv and at Pune from 17 to 30 ppbv (Fig. 3b).

Night values (mean of 2000 to 0700 h.) show a reversal of latitudinal gradient between Thiruvananthapuram and New Delhi with exception of higher value at Pune during all seasons. The night values range between 6 and 10 ppbv at Thiruvananthapuram, between 2 and 7 ppbv at New Delhi and at Pune between 7 and 27 ppbv (Fig. 3c).

The difference between day and night values is shown as diurnal change in Fig. 3d. This depicts that the day minus night value at Thiruvananthapuram and Pune is same during monsoon, but higher at New Delhi. During winter, diurnal change is the highest at Thiruvananthapuram and the lowest at Pune. In post-monsoon and summer, the day-night difference increases with latitude. In this case, the range of variation is from 2 to 15 ppbv.

3. ANNUAL CYCLE OF SURFACE OZONE OVER INDIA

Mean monthly ozone values for the three stations are plotted in Fig. 4a. It is seen from the figure that the annual maximum at New Delhi is attained in May-June and minimum value in January. From August to December the surface ozone amount is very low and steady, around 8-9 ppbv, with slight increase in October. From January the mean surface ozone value starts increasing from 6 ppbv attaining the highest value, about 19-20 ppbv, in May. From July, the surface ozone amount starts decreasing approaching a near minimum value in August.

The annual cycle at Pune shows a minimum value in July, August and September, the value being about 9 ppbv, from September the concentration starts increasing gradually up to December followed by a sharp increase from January reaching the maximum value in April

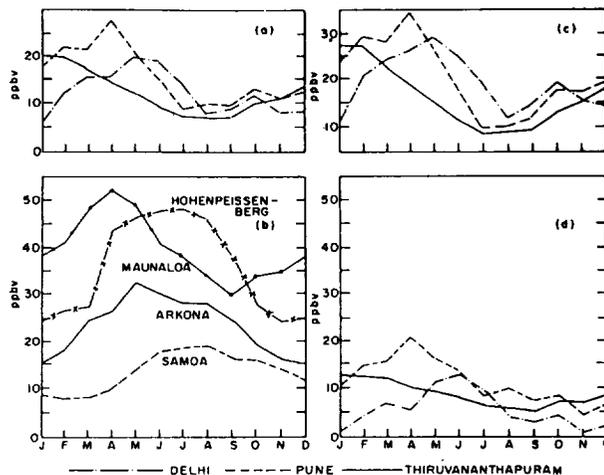


FIG. 4 - ANNUAL VARIATION IN SURFACE OZONE (1983-1985 Mean)
(a) INDIAN STATION, (b) SOME OTHER STATION FOR COMPARISON.
(c) DAY TIME AND (d) NIGHT TIME OZONE AMOUNT.

(25-26 ppbv). Again from April to July, there is almost a linear decrease. Similar to record of Delhi, Pune also shows a small increase in October.

The record of annual cycle at Thiruvananthapuram shows a smooth variation with maximum amount (19-20 ppbv) in January-February and a minimum (7-8 ppbv) in July-August-September. One noteworthy feature, as evident from the annual cycle at the three stations, is that during monsoon months July, August and September, the concentrations at all three stations are nearly equal and very low. The highest value at Thiruvananthapuram is attained in January-February, at Pune in March-April and at New Delhi in May-June. Thus the highest value in ozone occurs during dry months when the day's temperature is also maximum.

The low ozone amount during monsoon season points towards the ozone destruction by water vapour molecules and also towards a uniform mixed tropospheric air over the Indian subcontinent. The sharp increase beginning from January gives credence to stratospheric-tropospheric exchange through the discontinuity between the subtropical and tropical tropopause breaks and across the winter jet stream (sub-tropical jet stream) located at 300 hPa level. The increasing day temperatures also indicate more vertical mixing through deeper tropospheric layers. Thus the changes in surface ozone over Indian region are broadly explained by stratospheric-tropospheric exchange and change in mixing conditions in the boundary layer.

3.1 Comparison with annual variation at other stations

In Fig. 4b, annual cycles in surface ozone measured at Hohenpiessenberg (47.8°N, 11°E), Arkona (54.7°N, 13.4°E), Mauna Loa (19.5°N, 155.4°E) and Samoa (14°S, 170.3°E) have been shown. Concentration at Mauna Loa shows the maximum value (about 52 ppbv) during April and a minimum value (30 ppbv) in September. The gradient of increasing and decreasing trend from September to April and from April to September respectively is almost linear. The Mauna Loa observatory is located at an altitude of 3400 m. asl, above the trade wind inversion, and is more representative of the clean and free tropospheric ozone concentration. The highest and the lowest values can be taken to be representative of natural annual variations in tropospheric ozone. Mauna Loa record is very well compared with the records of Indian stations. The period of occurrence of maximum ozone at Mauna Loa and Pune (located in nearly same latitudinal belt) is in April, so also the absolute value at Pune is half of that observed at Mauna Loa. The range of annual cycle at New Delhi and Thiruvananthapuram is also well within the natural accountable limits as seen from Mauna Loa annual cycle.

The annual cycle of surface ozone at Arkona (Germany), a WMO Background Air Pollution Monitoring Network (BaPMON) station located on a bluff (42 m. asl), shows maximum value (32 ppbv) in May and minimum value (15 ppbv) in December. Comparing the annual variation over Indian stations, the values measured at New Delhi, Pune and Thiruvananthapuram are well below the ozone concentration recorded at Arkona.

Samoa, a coastal island station located in southern hemisphere tropics (14°S) near the sea level, shows that the maximum surface ozone (19 ppbv) occurs during July-August while minimum value (8 ppbv) is attained in February-March. From marine boundary layer ozone measurements from 32 ship cruises in the Atlantic Ocean between 80°N and 80°S, Winkler (1988) reported a northern hemisphere ozone concentration maximum of 30 ppbv between 25°N and 65°N. He also found a small maximum in the southern hemisphere of about 17 ppbv and a small minimum at the equator of about 14 ppbv. The low ozone amount at Samoa fits well with the above measurement in the SH tropics.

The record at Hohenpiessenberg shows very high value of surface ozone from March to November, the amount ranges between 25 and 48 ppbv and is certainly not accountable by natural processes but only by photochemical production in the troposphere.

3.2 Mean annual variation during day versus night time ozone amount

The mean monthly value for the day time (0800 to 1900 h.) and night time value (2000 to 0700 h.) have been plotted in Figs. 4c and 4d.

Day time values at New Delhi, Pune and Thiruvananthapuram show that the maximum value at Thiruvananthapuram is attained during January-February (about 26-27 ppbv) and the minimum occurs during July-September (9-10 ppbv). At New Delhi maximum value (about 29 ppbv) occurs during May and minimum (around 11 ppbv) in January. At Pune day time value shows the highest concentration (34 ppbv) in April while minimum occurs during July-August (about 10 ppbv). The annual cycle of day time ozone concentration (Fig. 4c) shows identical behaviour as depicted by monthly mean (day and night including) at the respective stations indicating that the major contribution towards daily mean comes from day time concentration.

Night time monthly variation at Thiruvananthapuram is similar to day time changes with maximum and minimum values of 12 ppbv and 5 ppbv respectively (Fig. 4d). At New Delhi, the minimum value (about 1 ppbv) occurs during November and January while maximum concentration during night (about 12 ppbv) occurs in June. At Pune minimum (about 4 ppbv) occurs in November while maximum occurs in April (about 20 ppbv). Night time changes in surface ozone show that the maximum value during night takes place in those months when the annual cycle also shows the highest value. But the night time minimum at New Delhi and Pune occurs in those months when the layers near the ground are cool and calm (probably associated with a temperature inversion) and they do not coincide with minimum of annual ozone cycle. But at Thiruvananthapuram maxima and minima in day and night time occur in same month and also coincide with the occurrence of the highest and the lowest values in annual cycle. This supports the view that near the equator the effect of stable surface layers is least or, in other words, the formation of stable and stratified layers near the ground is very rare in equatorial latitude.

3.3 Ozone amount in the free troposphere above the boundary layer

In order to have a rough estimate of ozone amounts in the free troposphere over Indian region, the day's maximum value (representative of free tropospheric ozone) and minimum value (representative of destruction near ground) has been plotted in Fig. 5 for the three Indian stations during 1983. Here again the near equatorial coastal station Thiruvananthapuram shows that the highest and the lowest ozone amount curves are almost parallel to mean. The minimum ozone shows the lowest value in July-August but this also is about 1.5 to 2 ppbv, while the highest value in the afternoon is obtained in the month of April, about 28 ppbv.

The envelopes of maximum and minimum ozone amount at Pune show one peak during February to April and another in November, the

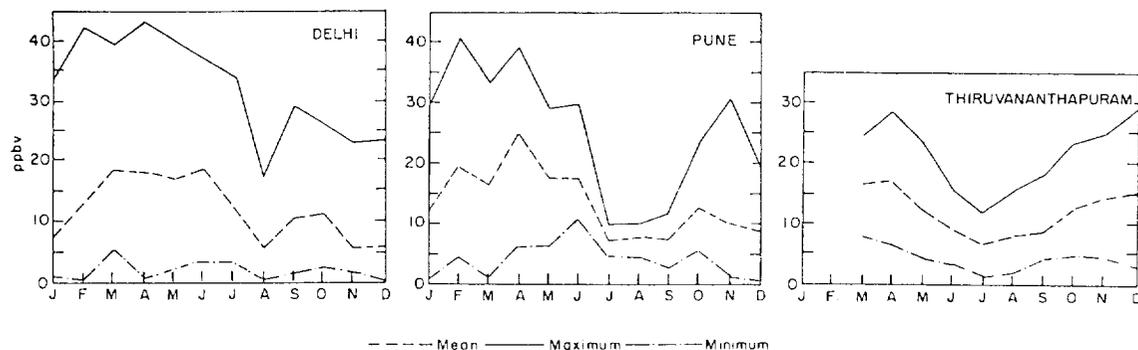


FIG. 5— RANGE OF MEAN, MAXIMUM AND MINIMUM SURFACE OZONE AMOUNT DURING 1983

values being of the order of 35 to 40 ppbv and 30 ppbv respectively. The profile of minimum ozone shows near zero value in December-January and higher night values from March to October with peak in June, about 10 ppbv.

The record at New Delhi shows that the free tropospheric ozone peak occurs from February to May, the value being about 40 ppbv accompanied by a sharp fall in August. But the decrease from April to November is linear except for August (low concentration during monsoon). The ozone profile of New Delhi indicates much better response to the injection of ozone rich stratospheric air into the troposphere during February to May months, due to its proximity near subtropical jet stream and tropopause break between the tropics and subtropics. In fact, New Delhi experiences double tropopause during winter season and the behaviour of ozone changes coincides roughly with the occurrence of maxima and minima in surface ozone in mid latitudes, e.g. Arkona. The profile of minimum ozone at New Delhi shows near zero night value from December to February and low value about 2 to 4 ppbv in other months.

The comparison of records at New Delhi, Pune and Thiruvananthapuram shows that both day and night values are higher at Pune. Though the Mauna Loa ozone amounts, representative of free tropospheric values in tropics, are still higher, but the sharp increase in ozone amount at Pune during April (seen in mean annual cycle - Fig. 4a) points to some tropospheric source. This point will be discussed further in next section.

4. TREND IN SURFACE OZONE VARIATION

From the hourly records of surface ozone, mean concentration for each month has been worked out at Thiruvananthapuram, Pune and New

Delhi for the years 1973, 1974 and 1975 and again for the years 1983, 1984 and 1985. These monthly mean values are plotted in Fig. 6. The period with no data has been shown by dotted curve in the figure.

It is seen from the figure that there are year to year variations at all the three stations, especially during 1984 when all the three stations recorded higher ozone concentration. Thiruvananthapuram and New Delhi also showed sharp fluctuations from month to month during 1974.

Year to year variations at Thiruvananthapuram from 1973 to 1985 indicate that both the lowest and the highest values during every year remained fairly stable. Thiruvananthapuram is a coastal station with lush green surroundings and devoid of heavy industries. Surface ozone record for the period gives an additional support that tropospheric ozone has not increased during these years. The highest value was around 17 ppbv and the lowest around 5-6 ppbv. New Delhi records show that annual maximum had remained steady at about 15 ppbv and the minimum 4-5 ppbv from 1973 to 1975. But from 1983 to 1985, the ozone amount shows a marginal increase in both minima and maxima values. The records at Pune also show that during 1973-74 maximum and minimum values were stable at 20 ppbv and 8 ppbv respectively. However, a slight increase in maximum value during 1975 is indicated though minimum value remained nearly same. The record from 1983 to 1985 does clearly bring out a gradual increase in the maxima and minima ozone amounts at New Delhi and Pune from year to year.

The increased industrialisation and human activities have resulted in increasing concentration of NO_x , CH_4 , CO and non-methane hydro-

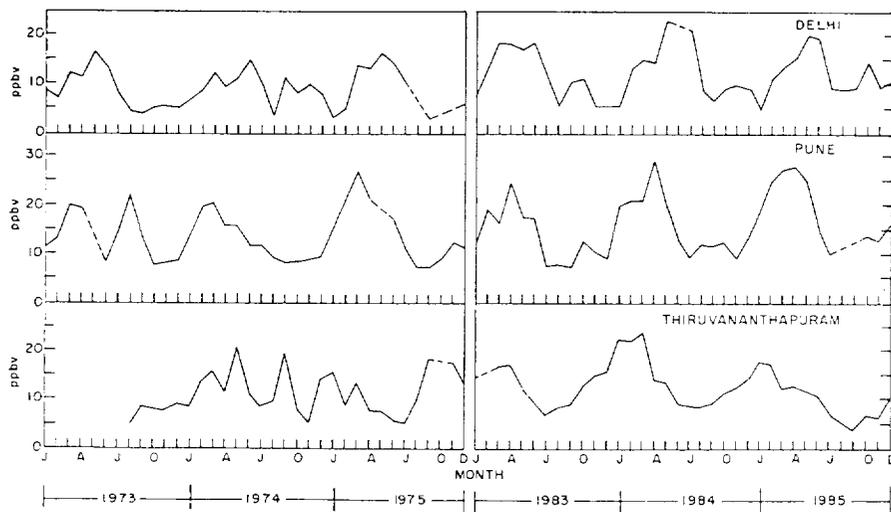


FIG 6 - TREND IN SURFACE OZONE AT INDIAN STATIONS

carbons (NMHC). The enhanced photochemical production in an atmosphere containing abundance of these anthropogenic gases is largely responsible for the increase in surface ozone concentrations (Penkett, 1984; Logan, 1985; Bojkov, 1986; Crutzen, 1988). Over New Delhi and Pune, the combustion processes and automobile exhaust produce large amounts of NO_x and other anthropogenic gases which help in photochemical production of ozone. Therefore, the year to year increase may be associated with tropospheric production. It was generally thought that Pune, by virtue of its location on a plateau at a height of 600 m asl, is a comparatively clean city but the surface ozone records show that the ozone amounts are higher at Pune compared to New Delhi. The high concentration of ozone during winter and summer seasons at Pune and the occurrence of maximum value in the evening hours (1800 LST) and quite high concentration up to midnight during summer point to transport of ozone rich air from some polluted site. From the wind speed and wind direction records at Pune, it is observed that wind speeds are quite high from 1700 to 2000 h. and the wind is blowing predominantly from WNW direction. This probably indicates transport of polluted air from industrial areas of Bombay.

The surface ozone data pertaining to three years 1983-85 is too small to fit a regression curve and to compute a quantitative value for trend analysis. This is more difficult because over and above the normal trend there are superimposed year to year variations. But three years' data from 1983 to 1985 show a positive (increasing) trend in surface ozone amount at Pune and New Delhi.

5. DISCUSSION AND CONCLUSION

5.1 The analysis of surface ozone data at the three Indian stations do indicate a diurnal and seasonal variation. The daily hourly data show that the minimum value in surface ozone is observed between 0700 and 0800 (LST) and the maximum value between 1400 and 1600 (LST). The night values are higher at Thiruvananthapuram but the day night difference is the lowest.

Ozone measurements at most rural continental stations show a diurnal cycle with sunrise minima and afternoon maxima (Parrish et al., 1986; Fehsenfeld et al., 1983). The diurnal variation observed at Indian stations follows similar pattern. Johnson et al. (1990) suggest that this diurnal cycles are driven by photochemical ozone production in daylight hours with loss to surfaces dominating at night. The diurnal change at Indian stations is presumed to be mainly due to meteorological processes, i.e. the convection currents set in during day time, causing greater mixing in the tropospheric layers near the ground. The mixing layer and the turbulence extend to higher tropospheric layers in the afternoon giving rise to higher surface ozone concentration. Even the turbulence caused by changes in wind speed during night or day is very well reflected in surface ozone records (Tiwari and Sreedharan, 1973). Higher ozone concentration during night at Thiruvananthapuram (though the average ozone is low) and near zero ozone value at New Delhi during night indicate the predominant role of turbulence and mixing processes.

5.2 The seasonal variations show that during monsoon season (June-August) the average ozone concentration is low and the values at all the

stations are almost identical (between 9 and 11 ppbv). The low concentration may be due to destruction by water vapour or be the result of low ozone air from the southern hemisphere. Low values associated with less diurnal change at Thiruvananthapuram and Pune, where the monsoon activity is for longer period and more vigorous than at New Delhi, suggest that the destruction by water vapour is important.

During winter season, the ozone amount at New Delhi is the lowest and that at Thiruvananthapuram the highest. This also supports the dominance of mixing processes over photochemical production, if any. During post-monsoon and summer seasons, Pune shows a higher concentration than New Delhi and Thiruvananthapuram. The highest value at Pune during summer occurs around 1800 h. and the pattern of decrease up to midnight suggests the transport of ozone rich air from an area of anthropogenic ozone production. The seasonal mean values at New Delhi and Thiruvananthapuram are almost identical varying between 8 and 16 ppbv in different seasons while the value at Pune shows a higher concentration, especially during post-monsoon and summer; the summer value is about 25 ppbv. The higher ozone value observed during summer at Pune indicates the possibility of tropospheric production due to anthropogenic gases.

5.3 Annual cycle over India shows that the maximum value (about 20 ppbv) at Thiruvananthapuram is attained in January-February, at Pune (about 27 ppbv) in April and at New Delhi (about 20 ppbv) in May-June, while the minimum values at Thiruvananthapuram (about 8 ppbv) and at Pune (9 ppbv) occur during monsoon season (June to August) and at New Delhi in January (about 6 ppbv). Comparison of the annual cycle at Indian stations with Mauna Loa (19.5°N) shows that the time of occurrence of maximum value coincides with Pune (18°N) in April while the minimum value at Mauna Loa occurs in September, but at Pune and Thiruvananthapuram it occurs during rainy season. The occurrence of maximum and minimum ozone amounts at New Delhi agree with that of Arkona (54°N). The ozone amount at Indian stations is less than half of the value observed at Mauna Loa and is well below the value found at Arkona. The concentration at Samoa (14°S) is comparable with the value measured at Thiruvananthapuram and also at New Delhi with phase lag in the time of occurrence.

Arpe et al. (1986) computed the turbulent kinetic energy (KE) distribution with respect to height, latitude and season from a long series of atmospheric data produced by ECMWF model. They showed that KE had two maxima in the NH summer but only a single maximum during austral summer at 30°S. In the NH a spring maximum is observed in all latitudes between equator and 80°N. For latitudes between 0° and 60°N, the

peak appears during May while north of 60°N the peak shifts to June and even to July (70°N). The minimum concentration occurs during fall or winter in most latitudes. North of the Polar front (60°N) there is an indication of higher winter concentration (Winkler P., 1989).

From the foregoing discussions it appears more logical that the annual cycle in ozone variation over Indian station is due to the natural cycle of stratospheric tropospheric exchange and the change of turbulent kinetic energy in the troposphere. However, some abrupt rise in surface ozone concentration at Pune (the maximum value in April) shows the contribution of tropospheric production.

5.4 Latitudinal variation over the Indian region is not very well demonstrated. During monsoon season there appears a slight positive gradient between Thiruvananthapuram (8°N) and New Delhi (28°N) but during winter season this gradient is reversed, indicating a rather well mixed troposphere (Fig. 3a) where the variation is governed by mixing conditions in the boundary layer. Winkler (1989) has shown from the result of 32 cruises that surface ozone has a positive gradient in the NH with minimum near the equator and higher value between 30°N and 50°N and another maximum between 60°N and 70°N.

5.5 Tropospheric production

the surface ozone records at three stations over India bring out the predominant role of meteorological factors and turbulent mixing processes in the diurnal, seasonal and annual cycles. But from the comparison of year to year data from 1973 to 1975 and from 1983 to 1985, there appears to be slow increase in year to year surface ozone amounts at Pune and New Delhi. However, the record at Thiruvananthapuram does not indicate any change from 1973 to 1985. Some sharp increase in ozone amount recorded at Pune during March-April calls for additional source of production in the troposphere. The forenoon maximum is associated with a temperature inversion near the ground, trapping the gases from the automobile exhaust and factory products. With the sunrise and breaking up of inversion, a maximum in the ozone amount is observed due to in situ production of ozone. It is noted that in case of anthropogenic production, the forenoon maximum becomes the main maximum of the day and occurs near the local noon. The seasonal maxima at Pune during summer at 1800 (LST) appear to be due to transport of air from a polluted site.

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